

Sterols in aerosols, surface microlayer and subsurface water in the North-Eastern tropical Atlantic

Aerosols
North-Eastern tropical Atlantic
Sea water
Sterols
Surface microlayer

Aérosols
Eau de mer
Microcouche de surface
Océan Atlantique tropical Nord-Est
Stérols

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ABSTRACT

Aerosols, surface microlayer and subsurface water samples were collected in the north-eastern tropical Atlantic. Sterol analyses, both for particulate and for dissolved sterols, were carried out by gas chromatography and combined gas chromatography-mass spectrometry for aerosols and for microlayer and seawater samples. The amounts of sterols detected in the aerosols of the marine atmosphere vary within the range 2.2-9.2 ng . m⁻³, concentrations being related to wind speed, which was monitored during the cruise.

The compositions of aerosols and particulate matter from seawater are similar, with a large predominance of cholesterol over other sterols, among which brassicasterol, β -sitosterol and 22-dehydrocholesterol are the main components. The ejection into the atmosphere of microlayer water containing both dissolved and particulate fractions is discussed with reference to factors controlling the exchange of organic matter through the sea-air interface and the impact of such biologically interesting compounds on the ocean-atmosphere-continent cycle.

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RÉSUMÉ

Stérols dans les aérosols,
la microcouche de surface et l'eau sous-jacente
en Atlantique tropical Nord-Est.

Les aérosols, la microcouche de surface et l'eau sous-jacente ont été prélevés dans l'Atlantique tropical Nord-Est. Les stérols ont été analysés par chromatographie en phase gazeuse couplée à la spectrométrie de masse dans les aérosols, la microcouche de surface, et l'eau de mer, pour la matière organique en solution et associée aux particules. La quantité de stérols dans l'atmosphère marine varie de 2,2 à 9,2 ng . m⁻³, les concentrations les plus élevées étant notées par vent fort.

La composition des stérols des aérosols est voisine de celle de la matière en suspension de l'eau de mer. Elle est caractérisée par la prédominance du cholestérol sur d'autres composés, parmi lesquels le brassicastérol, le β -sitostérol et le 22-dehydrocholestérol. L'éjection de la microcouche avec ses composés dissous et ses particules dans l'atmosphère est discutée en examinant les facteurs qui contrôlent les échanges de matière organique à l'interface mer-air, et l'impact de tels composés à action biologique dans le cycle océan-atmosphère-continent.

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INTRODUCTION

Sea water sterols, either dissolved or associated with suspended matter, have been investigated during recent years: by Kanazawa and Teshima (1971) in Japan; Gagosian (1975, 1976), Gagosian and Heinzer (1979) in the United States; Saliot and Barbier (1973), Saliot (1975), Tusseau *et al.* (1978), Boussuge *et al.* (1980 a), Tusseau (1980) in France.

Due to their high degree of stability in the marine environment and to their diversity, sterols are useful ecological markers. Relative abundances of C-27 and C-29 sterols may be used to determine the proportions of terrigenous and autochthonous organic materials in marine waters and sediments (Huang, Meinschein, 1976, 1979; Boutry *et al.*, 1979; Boussuge *et al.*, 1980 b).

During the "Midlante" cruise in the eastern tropical Atlantic, aerosols, surface microlayer and subsurface water were collected simultaneously, every precaution being taken to avoid shipboard contamination. For the first time to our knowledge, a comparative analysis was performed of the sterols present in each fraction, distinguishing between dissolved and particulate matter for the surface microlayer and subsurface water.

This article deals with the significance of sterol concentrations and distributions (obtained during a systematic study of lipids such as fatty acids and hydrocarbons [Marty *et al.*, 1979]), as ecological and sea-air exchange process indicators.

EXPERIMENTAL

Sampling

Samples were obtained during the "Midlante" cruise of the R/V "Jean Charcot", in May 1974 (Fig. 1). The atmospheric aerosol sample A1 was collected along the

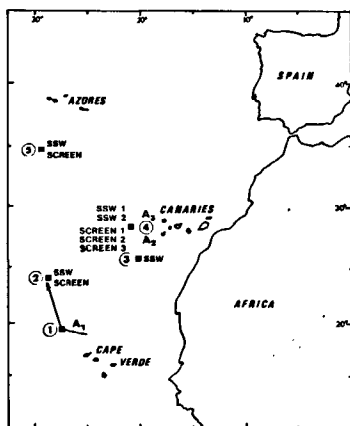


Figure 1
Sampling sites. A1, A2 and A3 are aerosol samples; screen refers to surface microlayer samples taken with the Garrett screen, and SSW denotes subsurface water samples. Numbers within circles refer to station numbers.

Sites de prélèvement avec les 3 échantillons d'aérosols A1, A2 et A3. Screen désigne les échantillons de microcouche prélevés au tamis de Garrett et SSW les échantillons d'eau sous-jacente. Les stations sont identifiées par les chiffres entourés d'un cercle.

cruise track denoted by the arrow, covering the hydrographic stations 1 and 2. The other aerosol samples A2 and A3 were collected during small legs around station 4. These samples were obtained by filtering large volumes of air (1 200-1 900 m³) through 15-cm Whatman GF/B glass fibre filters in metal holders placed 8 m forward of the ship's bow, and 8 m above sea level. The pump was operated several metres behind the filter holders. To minimize contamination, the pump was stopped during cross or back wind, as a result of constant wind direction monitoring. At no time was the pump in operation, while the ship was stopped on station.

Water samples were collected at the beginning of each stop on a hydrographic station (Fig. 1), from a rubber Zodiac boat located 1-2 km upwind of the ship. Subsurface water samples (100 l) were obtained by plunging a 25 l glass bottle several times below the water surface.

Surface microlayer samples (20 l) were taken, using the Garrett (1965) technique. A stainless steel screen made of 0.36 mm diameter wire with 1.25 mm square openings in the mesh, was immersed vertically and removed horizontally, sampling a film approximately 0.44 mm thick (Marty, 1974). The collected film was then drained into a glass bottle.

Filtration of microlayer and subsurface water samples

On board ship, both microlayer and subsurface water samples were filtered through preextracted Whatman GF/C 15-cm diameter glass fibre filters. These filters collect particles with a diameter greater than $\sim 1 \mu\text{m}$. Although, operationally, this procedure only defines the particulate fraction of the sterols in the water samples, the possibility that unesterified sterols in the dissolved state might adsorb onto the glass fibre surface must be kept in mind. The ratio of free to esterified sterols for western North Atlantic Ocean samples is approximately 2, in both surface and deep water (Gagosian, 1975). Saliot (1975) has observed from laboratory studies that the adsorption of fucosterol propionate on Millipore 0.45 μm filters amounts to 20-25% of the dissolved sterol concentration. As the retention of dissolved organic material is greater on Millipore filters than for glass fibre (Quinn, Meyers, 1971), and by comparison with other experiments, the retention of dissolved sterols by Whatman GF/C filters can be estimated in the range 5-10%. As the amounts of total sterols found on the filter and in the filtrate are comparable, it seems fair to conclude that most of the sterols retained by the filter are in particulate form.

Extraction and isolation of sterols

The isolation of sterols from lipid fractions has already been reported (Saliot *et al.*, 1978; Marty *et al.*, 1979). Briefly, water samples were extracted 3 times with doubly distilled chloroform, dried over CaCl₂, concentrated on a rotary evaporator (at 40°C), and placed in a freezer (-20°C) in the dark for shore-based analysis. Filters were extracted in a soxhlet using a 1 : 1 mixture of

benzene-methanol. Despite repeated analysis over a period of months, and even after a long conservation time, during which samples were maintained in the dark at very low temperatures ($< -20^{\circ}\text{C}$), significant changes in the sterol composition were never observed. The extracts were saponified; the total sterols obtained from the unsaponifiable fraction through SiO_2 thin-layer chromatography were acetylated with pyridine-acetic anhydride.

Gas chromatographic analysis and gas chromatography-mass spectrometry

The gas chromatograph—a Varian 1440 with a flame ionization detector—was used with 2 columns ($2\text{ m} \times 3.4\text{ mm}$ i.d., glass columns packed with 2% OV 101 on chromosorb WHP 100-120 mesh, or packed with 1.5% OV 225 on chromosorb 100-120 mesh). The carrier gas (He) flow rate was $20\text{ ml} \cdot \text{min}^{-1}$. The column temperatures were 250°C for OV 101 and 220°C for OV 225. Sterols were identified by comparison of the relative retention times (RRT), with those of known standards (provided by the M.R.C., Great Britain), on both columns. The peak area corresponding to each sterol was measured by means of a planimeter, and concentrations were obtained by comparison of sample peak areas with that of known amounts of cholestane used as internal standard.

Mass spectra were obtained using a Girdel 3000 gas chromatograph, equipped with a glass capillary column coated with SE 52 ($40\text{ m} \times 0.25\text{ mm}$ i.d., temperature programmed from 230 to 270°C at $0.2^{\circ}\text{C} \cdot \text{min}^{-1}$), coupled to a Ribermag R 10-10 spectrometer-Sidar computer.

The utilization of 3 stationary phases did not allow for a distinction between all C-24 epimers, but permitted separation of β -sitosterol (RRT relative to cholesterol on OV 101 and OV 225: 1.56 and 1.76) and its epimer clionasterol (RRT on OV 101 and OV 225: 1.64 and 1.57).

Table 1

Sampling references (date and location); meteorological observations: wind direction and speed ($\text{m} \cdot \text{s}^{-1}$), atmospheric pressure (mean during the sampling time, about 48 hours for aerosol collection); sterol concentrations in aerosols ($\mu\text{g} \cdot \text{m}^{-3}$), subsurface water and microlayer, both for dissolved (D) and particulate (P) forms ($\mu\text{g} \cdot \text{l}^{-1}$); * (D+P).

Coordonnées de l'échantillonnage (date et site); observations météorologiques : direction et vitesse du vent ($\text{m} \cdot \text{s}^{-1}$), pression atmosphérique moyenne pendant l'échantillonnage, durée : 48 heures pour les aérosols; concentrations en stérols dans les aérosols en $\mu\text{g} \cdot \text{m}^{-3}$, concentrations en stérols dissous (D) et particulaires (P) dans l'eau de mer et la microcouche en $\mu\text{g} \cdot \text{l}^{-1}$; * (D+P).

Date	Station (Fig. 1) and sample reference	Location		Meteorological observations, wind direction and speed ($\text{m} \cdot \text{s}^{-1}$), atmospheric pressure (mbar), average	Aerosols ($\mu\text{g} \cdot \text{m}^{-3}$)	Subsurface water ($\mu\text{g} \cdot \text{l}^{-1}$)			Microlayer ($\mu\text{g} \cdot \text{l}^{-1}$)		
		Longitude	Latitude			D	P	D/P	D	P	D/P
26/4/74	1	19°36'N	27°26'W	NE, 11 $\text{m} \cdot \text{s}^{-1}$ (1016)	—	—	—	—	—	—	—
26/4-28/4/74	A1	—	—	NE, 9.2 $\text{m} \cdot \text{s}^{-1}$ (1019)	9.2×10^{-3}	—	—	—	—	—	—
28/4/74	2	24°03'N	28°56'W	E-NE, 7.2 $\text{m} \cdot \text{s}^{-1}$ (1020)	—	3.00	1.53	2.0	—	0.68	—
1/5/74	3	25°57'N	20°20'W	NE, 11.3 $\text{m} \cdot \text{s}^{-1}$ (1021)	—	4.08	0.84	4.9	—	—	—
5/5/74	4.1	28°19'N	21°00'9"W	NE, 7.6 $\text{m} \cdot \text{s}^{-1}$ (1021)	—	6.91	0.54	12.8	1.70	—	—
5/5-7/5/74	A2	28°19'N	21°00'9"W	NE, 8.6 $\text{m} \cdot \text{s}^{-1}$ (1021)	6.0×10^{-3}	—	—	—	—	—	—
10/5/74	4.2	28°19'N	21°00'9"W	NE, 2.7 $\text{m} \cdot \text{s}^{-1}$ (1021)	—	0.45	0.16	2.8	3.86	2.91	1.3
9/5-11/5/74	A3	28°19'N	21°00'9"W	N-NE, 3.1 $\text{m} \cdot \text{s}^{-1}$ (1021)	2.2×10^{-3}	—	—	—	—	—	—
12/5/74	4.3	28°19'N	21°00'9"W	N, 1.4 $\text{m} \cdot \text{s}^{-1}$ (1020)	—	—	0.54	—	1.86	—	—
15/5/74	5	34°43'N	29°34'W	SW, 8.1 $\text{m} \cdot \text{s}^{-1}$ (1018)	—	7.7	0.3	22.6	15.9	5.0	3.2

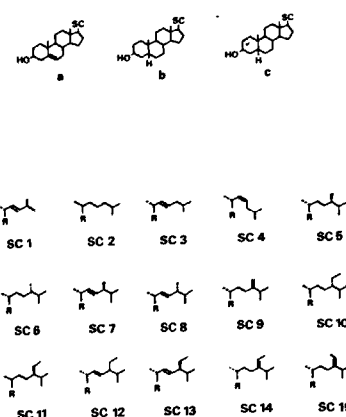


Figure 2
Structures of sterols commonly encountered in the marine environment.
Structures des principaux stérols rencontrés en milieu marin.

Sterol structures of common marine sterols are shown in Figure 2.

Blanks, precision and detection limits

Contrary to the filters used for sea water filtration, the GF/B filters used for aerosol collection were not pretreated. Comprehensive aerosol blanks were taken by subjecting unused filters to the same conditions of storage, transport and handling as the sample filters (except filtration of air), including mounting in the sample holder on the ship's bow. No sterol could be detected after analysis of these filters as described above.

The lower limit of sterol detectability is 0.1 ng of each sterol per litre of sea water in a 20-100 l sample volume, and around $0.01\text{ ng} \cdot \text{m}^{-3}$ for a 1000 m^3 of air volume. Analytical precision, taking into account extraction, chemical steps during sample work-up and the gas liquid chromatography analysis, has been estimated at 30% for sterols. The reproductibility of replicate samples

collected in a homogeneous water mass is $\pm 10\%$, close to that determined by Gagosian and Nigrelli (1979). But the reproductibility for the relative composition of sterols is better than 1% for each sterol, permitting a really good comparison of samples collected in various areas for their sterol distribution.

RESULTS AND DISCUSSION

Sterol concentrations

The total, free and esterified sterol concentrations found in the aerosols, in the microlayer and in the subsurface water are listed in Table 1. Seawater concentrations vary from 0.5 to 7.7 $\mu\text{g.l}^{-1}$ concerning the dissolved fraction, and between 0.2 and 0.8 $\mu\text{g.l}^{-1}$ in the particulate matter. The concentrations reported here are in the same range as those indicated by different authors for Atlantic oceanic waters (Table 2).

The dissolved (D)/particulate (P) sterols ratio is between 2 and 22. This value is close to the total organic carbon dissolved/particulate ratio in seawater as reported by Menzel (1974). The sterols found in the microlayer vary from 1.7 to 15.9 $\mu\text{g.l}^{-1}$ for the dissolved fraction and from 0.7 to 5.0 $\mu\text{g.l}^{-1}$ for the particulate fraction. The D/P ratio relative to the microlayer is somewhat lower than that for subsurface water.

Attempts made to correlate total sterol concentrations with biological parameters such as chlorophyll *a* or zooplankton biomass (Goutx, 1978; Tusseau, 1980) do not give a statistical relationship; but generally, in the concentration range observed for Mediterranean waters collected at the same station during an eighteen-month period (0.06-18 $\mu\text{g.l}^{-1}$ for dissolved sterols, 0.01-3 $\mu\text{g.l}^{-1}$ for particulate sterols), the maxima for sterol concentrations are observed simultaneously with the zooplankton biomass maxima. The concentration variability is thus probably controlled by the biological productivity of marine organisms.

The microlayer is relatively depleted in sterols during the first part of the cruise. At station 4, in association with low wind speeds (Table 1), the microlayer becomes enriched in sterols, after May 10. The enrichment for samples 4.2 and 4.3 is in the range 6-8. At station 5, the enrichment factor is still higher (~ 15) in particulates than in the dissolved fraction (~ 2). Such an enrichment may be due to the presence of living organisms in the microlayer neuston (Harvey, 1966; Champalbert, 1975; Liss, 1975; Wangersky, 1976), and also to detritic organic matter composed of fragments or cells from dead organisms. It is already known that the concentration of particulate organic carbon is about 10 times higher in the microlayer than in subsurface water (Williams, 1967; Liss, 1975). Following Williams (1967) and Sieburth *et al.* (1976), this value is only 2 times higher for the dissolved carbon. Averages indicate an enrichment in total sterols (dissolved plus particulate) of about 2, similar to the results already noticed for fatty acids (Quinn, Wade, 1972; Duce *et al.*, 1972) and hydrocarbons (Duce *et al.*, 1972; Wade, Quinn, 1975; Marty, Saliot, 1976; Marty *et al.*, 1978).

Sterol concentrations in the aerosols vary between 2.2 and 9.2 ng.m^{-3} (Table 1). The highest value was obtained in rough sea conditions. Thus, the A1 aerosol sample was collected with high wind speed (average: 9.2 m.s^{-1} , with maxima of about 11 m.s^{-1}). The enrichment of the atmosphere in suspended materials, generally associated with the strength of winds and consequent bubble bursting after injection of air into the microlayer, is equally noticeable, as far as concentrations of fatty acids and hydrocarbons are concerned (Marty *et al.*, 1979).

The aerosols contain about 2 $\mu\text{g.m}^{-3}$ of organic carbon (Marty *et al.*, 1979). Thus, with a value of 1.2 as conversion factor for the ratio organic carbon/sterol in mass, the sterols would represent ca. 0.2% of the total organic carbon, that is a value close to that found for subsurface water.

Table 2
Sterol concentrations reported for Atlantic waters.
Concentrations en stérols d'eaux de l'océan Atlantique.

Sterols analysed	Area	Concentration range ($\mu\text{g.l}^{-1}$)	Reference
Dissolved total (free and esterified) sterols	eastern equatorial	4-15	Saliot and Barbier (1973)
Dissolved and particulate free sterols	western north	0.2 -1.3	Gagosian (1975)
Dissolved and particulate total sterols	western north	0.3 -1.3	Gagosian (1975)
Dissolved and particulate free sterols	Sargasso sea	0.02-0.35	Gagosian (1976)
Dissolved total sterols	Cariaco trench	0.2 -1.2	Tusseau <i>et al.</i> (1978)
	western north tropical		
Particulate total sterols	Cariaco trench	0.01-0.06	Tusseau <i>et al.</i> (1978)
	western north tropical		
Dissolved and particulate free sterols	western north	0.1 -0.4	Gagosian and Nigrelli (1979)
Dissolved total sterols	eastern north	0.4 -7.7	This work
Particulate total sterols	eastern north	0.2 -0.8	This work

Sterol compositions

The detailed sterol compositions of the 3 aerosol and seawater samples are shown in Table 3. As mentioned in the experimental section, among the C-24 epimers, only the β -sitosterol-clionasterol pair is resolved under the GC conditions described above. Clionasterol (structure 10a) was not identified in any of our marine samples.

Sterol inputs at the surface of the oceans are of various kinds, including concentrations of total sterols and specific compounds. Recent reviews have appeared on sterols in marine organisms (Goad, 1976; Morris, Culkin, 1977; Goad, 1978), marine plants (Heftmann, 1971; Patterson, 1971) and fungi (Weete, 1973). Bacteria do not generally produce sterols, but they do utilize sterols as electron donors (Eyssen *et al.*, 1973).

For open sea waters, the main sources of sterols are phytoplankton and zooplankton. Although marine sterols range from C-25 to C-30, the majority in the case of planktons have a carbon range of C-27-C-29, with C-27 predominant (Boutry, Baron, 1967; Boutry, Jacques, 1970; Tusseau, 1980). For some species, the sterol distribution is quite original; for example, a C-28 sterol—brassicasterol—is the main sterol in the marine diatoms *Cyclotella nana*, *Nitzschia closterium* (Kanazawa *et al.*, 1971) and *Nitzschia alba* (Tornabene *et al.*, 1974).

Organic matter of terrestrial origin enters the marine environment through river runoff or aeolian transport on particulates. C-29 and C-27 sterols are the predominant sterols in higher plants (Huang, Meinschein, 1976; Nishimura, Koyama, 1976; 1977) and in soils (Meinschein, Kenny, 1957). With the aid of calculations based on the relative abundances of C-29 and C-27 sterols, the significant difference between sterol distributions in higher plants and marine planktons permits use of these compounds as ecological markers (Huang, Meinschein, 1976, 1979; Bousuge *et al.*, 1980 b).

Particulate sea water sterol distributions

Cholesterol, C-27 sterol, predominates in all the particulate samples collected throughout the cruise, both from surface and from microlayer waters (Table 3). The percentage range varies from 37 to 78%. The marine contribution from various planktonic organisms is also revealed by the relative importance of other compounds; brassicasterol and/or crinosterol always account for more than 5% (St. 4.2), generally for about 10%, a little higher in the case of station 2 (13.7%). In order of decreasing importance the two C-27 sterols, 22-*cis* and -*trans* dehydrocholesterol, account for a significant part of total sterols varying from 5% for station 4.2 (microlayer) to 19 and 23% for station 5 (microlayer and subsurface water).

The importance of C-29 sterols (β -sitosterol, fucosterol and isofucosterol) is of the order of 5-8%, except for the first stations 2, and 4.1, characterized by higher percentages of C-29 sterols—(15-30%)—, and especially β -sitosterol. What is the origin of the C-29 sterols in these

Table 3
Percentage compositions of sterols from Midlante samples (North-Eastern Atlantic). D=dissolved sterols; P=particulate sterols. () sterol structures, see Figure 2.*
Compositions relatives des stérols des échantillons Midlante, en provenance de l'océan Atlantique Nord-Est; D=stérols dissous; P=stérols particulaires; () structures des stérols (fig. 2).*

Sterol	Subsurface water			Aerosols			Subsurface water			Microlayer			Subsurface water						
	A1	2D	2P	2P	2P	A2	A3	4.1D	4.1P	4.2D	4.2P	4.3P+D	4.1D	4.2D	4.2P	4.3D	5D	5P	
24-norcholestadienol	-	-	-	-	-	-	-	0.5	0.8	5.2	-	-	-	-	-	-	0.9	2.4	0.8
Coprostanol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1.8	-
22- <i>cis</i> dehydrocholesterol	-	-	1.7	5.6	-	-	-	-	3.2	-	4.2	2.2	-	0.8	1.3	1.5	-	9.7	0.7
22- <i>trans</i> dehydrocholesterol	-	-	6.2	9.3	-	-	5.1	1.5	5.3	-	4.2	3.1	-	0.9	3.3	2.2	-	9.3	0.8
Cholesterol	40.9	38.3	77.9	40.4	78.3	65.5	21.7	37.2	37.2	18.9	56.2	34.0	22.2	29.7	76.5	35.3	16.0	56.2	20.6
Cholestanol	5.7	1.7	-	2.7	7.6	12.0	0.3	1.2	5.9	3.2	5.9	3.3	7.2	5.8	4.0	3.3	1.8	2.9	2.2
Brassicasterol and/or crinosterol	40.8	1.5	4.9	13.7	1.1	1.9	0.4	10.8	6.9	10.6	9.4	-	-	2.9	-	13.9	3.1	9.2	1.1
22- <i>trans</i> dehydrocholestanol	-	-	-	2.5	-	-	0.4	1.2	-	-	-	-	-	-	-	-	-	0.7	3.8
24-methylcholesterol	-	-	1.5	1.8	3.6	4.3	0.8	2.6	4.0	10.4	-	-	5.5	6.4	1.9	-	2.1	2.2	3.8
Campesterol and/or dihydrobrassicasterol	-	-	5.7	1.3	1.2	-	1.3	2.0	2.8	-	-	4.7	-	3.6	1.6	3.7	1.4	1.0	4.9
Stigmasterol and/or poriferasterol	-	-	-	1.7	3.9	-	1.6	3.9	-	-	-	2.5	1.2	-	-	2.2	2.0	1.0	5.9
Fucosterol	0.6	-	-	1.7	1.2	-	-	-	9.7	1.8	-	-	23.9	-	1.5	-	5.0	1.6	-
β -sitosterol	12.0	52.8	4.8	8.8	8.2	11.2	58.9	24.2	33.8	6.7	40.2	-	38.3	49.5	4.6	37.9	48.1	2.0	34.8
Isofucosterol	-	-	-	4.7	-	-	12.6	6.6	15.5	-	-	-	-	-	-	-	18.1	-	20.6

samples? Two hypotheses may be advanced: it is known that NE winds like the Harmattan transport terrigenous contributions over the entire Atlantic Ocean (Simoneit, 1977). Such high incidences of C-29 sterols may thus be associated with atmospheric dusts, which also introduce dissolved organic matter into the sea water, leading to a terrigenous trace which is also visible in the dissolved fraction. A runoff input cannot be totally rejected, even in this area far from potential river inputs, since terrigenous material can be transported over considerable distances in the open sea; this is demonstrated for example by Boussuge *et al.* (1980 *b*), concerning dissolved organic matter originating from Amazon river inputs along the Brazilian coasts.

Coprostanol is present at low levels (2-4%), but only in some particulate samples. This observation, corroborating data obtained in a Mediterranean bay (Tusseau, 1980), indicates that this sterol is not present in the dissolved state, as is the case with other sterols, and is associated with particulates, trace of a bacterial activity either marine or related to faecal pollution (Kanazawa, Teshima, 1978).

Dissolved sea water sterol distributions

The first interesting observation to be made from Table 3 is that the distribution of dissolved sterols is significantly different from that of particulate sterols, leading to the concept that the bulk of dissolved organic matter is supplied not only by planktonic marine inputs, but also by different marine or terrigenous inputs.

For the dissolved sterols in either subsurface or microlayer samples, a C-29 sterol, β -sitosterol predominates, in the range 34-53%, before cholesterol. The other C-29 sterols, fucosterol and isofucosterol, which are particularly abundant in brown algae for the fucosterol (Patterson, 1971) or in green algae (Knights, 1967; Gibbons *et al.*, 1968; Doyle, Patterson, 1972), are present in significant amounts at stations 4 and 5, and not in the particulates. Fucosterol has been detected in different oceanic waters, as related by Gagosian (1975) for the western North Atlantic Ocean (3-8% of total dissolved and particulate sterols). The possibility of using these compounds as tracers for benthic inputs remains to be confirmed by further samplings; but the observations related by Tusseau *et al.* (1978) concerning the fate of Amazon river inputs, which show a good preservation of C-29 sterols – whether β -sitosterol or fucosterols – in the water, prove that this markage can be transported over very great distances from the river mouth or the algal reefs.

The dissolved fraction contains extremely small amounts (some %) of other sterols such as 22-dehydrocholesterol, cholestanol, brassicasterol and/or crinosterol, 22-dehydrocholestanol, 24-methylencholesterol, campesterol and/or dihydrobrassicasterol and stigmasterol and/or poriferasterol.

Although the sterol compositions of subsurface and microlayer are generally very similar, some differences are remarkable: for example, at station 4.1, the microlayer is considerably enriched in dissolved fucosterol (23.9%), and not in isofucosterol.

Aerosol sterol distributions

Samples A2 and A3 have very similar compositions, and are characterized by a high percentage of cholesterol (65-78%), a low contribution of β -sitosterol (8-11%) and a non negligible percentage of cholestanol (8-12%). Two observations may be made; the composition of the two aerosol samples collected at the same station, A2 and A3, is close to that of particulate matter of the microlayer, and very different from the dissolved fraction, which is highly enriched in C-29 sterols. The other feature to be noted is the apparent relative enrichment of the atmospheric samples in cholestanol. The microlayer and underlying waters have low percentages of cholestanol. To the extent that we can consider the presence of stanols to be indicative of a bacterial activity, as proposed by different authors, such as Eyssen *et al.* (1973) or Nishimura and Koyama (1977), the aerosol material is altered by an intense bacterial activity. Since bacteria are highly enriched in the sea surface microlayer (Sieburth, 1971; Blanchard, 1978), they are ejected during bubbling into the atmosphere either in the aerosol, which constitutes a microecological niche (Wangersky, 1976) or either on the fiber glass filter, they find specifically favourable conditions (a support and organic matter to consume) for very rapid growth. In the absence of bacterial population determination on filters, it is not possible to evaluate the activity due to natural bacteria ejected into the atmosphere, and the effect of concentration related to the sampling system used.

The aerosol sample A1 is quite different, and is characterized by large quantities of a C-28 sterol, brassicasterol, which may be accompanied by traces of crinosterol. As brassicasterol has been previously found as the dominant sterol in some diatoms (Kanazawa *et al.*, 1971; Rubinstein, Goad, 1974; Tornabene *et al.*, 1974; Huang, Meinschein, 1979), we can propose an explanation for this composition: in relation to very high wind speeds (mean: 9.2 m.s^{-1} , with maxima approaching 11 m.s^{-1} over a period of more than 12 hours), diatoms may have been ejected from the microlayer and collected on the filters. This possibility has been confirmed by different authors, including Sieburth *et al.* (1976).

The sea-atmosphere exchange process

Due to the absence of the atmospheric vapour phase organic material characterization, it is not possible to evaluate the total budget of the sea-atmosphere exchange processes. But we can advance some explanations, in connection with other results relative to fatty acids or hydrocarbons (Marty *et al.*, 1979), considering the difference of composition between the dissolved and the particulate sterols, an unusual fact in marine organic chemistry. Generally, as for other lipids, the dissolved material – in greater absolute amounts – has a composition very similar to that of the particulate fraction. This fact is worthy of consideration in relation to evaporation and bubbling processes.

Sterols are present in sea water as free and esterified forms. Depending on the molecular weight and the

polarity of sterols and sterol esters, evaporation of the lighter and less polar compounds may explain certain of the C-27-C-29 distribution differences. In this hypothesis, the C-27 predominance in the aerosols may be due to the fact that C-27 sterols are present in a predominant free or light ester form. This can correspond to a high molecular form for C-29 sterols of continental origin. The same hypothesis would also partly explain the dissolved/particulate sterol distribution difference for superficial waters. If, in fact, C-27 sterols are selectively transferred into the atmosphere through evaporation, this could lead to the C-29 enrichment for dissolved sterols.

The second hypothesis involves selective particulate transfer through bubble bursting, as suggested first by Tusseau *et al.* (1980), in view of the similar composition between particulate matter and aerosols. In this case, particulates and not the entire microlayer (water and particulates) would be ejected selectively during bubble bursting. If this transfer exists, as is suggested by the sterol distribution of the first A1 aerosol sample, collected under rough sea conditions and containing high percentages of typical planktonic sterols, the process could have a great importance in the transfer of chemical species in the entire ocean-atmosphere-continent cycle.

Is there any possibility of the sterols detected in the atmosphere being transported over very long distances?

Probably yes, but this matter warrants further investigation, and the collection of organic matter for lipid analysis at different levels over the sea surface; but since among the various organic molecules identified in sea water, certain steroids are highly biologically active components in trace amounts, the bioecological situation resulting from the ejection of sterols into the aerial space from the micronic fraction of the sea is of interest.

The chemistry of three quarters of the planet is formed at the air-sea interface, where a density of phenomena, a higher content of unicellular organisms and a richer accumulation of organic substances are all to be found. The fact that particulate matter from this film could be more determinant than dissolved matter is of great importance.

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